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"INVESTIGATIONS IN THE FIELD OF COMPLEX FLUORIDES

OF TANTALUM AND COLUMBIUM."

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/A Digest/

/This is a communication from the Analytical Laboratory of the Institute of General and Inorganic Chemistry of the Academy of Sciences, USSR/
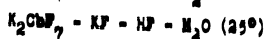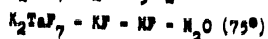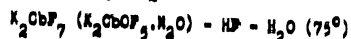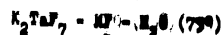
In a prior article by the same authors (1), results of investigations on solubilities in four ternary systems K_2TaF_7 (K_2CbF_7) - KF - H_2O and $KTaF_6$ $(KCbF_6)$ - HF - H_2O at $25^\circ C$ were reported. The possibility of isolating the new salts $KTaF_6$ and $KCbF_6$ at concentrations of KF exceeding 40% was shown. Laubengayer and Polzer (2) have prepared $NaCbF_6$ by combining CbF_5 with NaF in anhydrous HF. Highly concentrated KF solutions do not present any advantage for the separation of tantalum and columbium as compared with dilute HF solutions. The conclusions of Marignac (3) and of Ruff and Schiller (4) have been confirmed thereby. These investigators have recommended the known method of separating tantalum and columbium in the form of their double salts with potassium fluoride. The possibility of obtaining columbium free K_2TaF_7 in this manner was demonstrated by Zverev and Meerson (5). The problem of separating tantalum and columbium in the form of their potassium double fluorides was not solved thereby, however, because complete data on the behavior of both K_2TaF_7 and K_2CbF_7 in solutions containing simultaneously KF and HF in various proportions are necessary for that purpose. Only fragmentary data on the subject were available and the present investigation was carried out with the purpose of filling that gap. Additional work on the subject by Babaeva and Klyachko-Gurvich (6) may be cited.

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From the behavior of the double salts in question at 75° is significant. Therefore solubilities in the following systems were determined:

K_2TaF_7 - KF - H_2O (75°)

K_2CbF_7 ($K_2CbOF_5.H_2O$) - HF - H_2O (75°)

K_2TaF_7 - KF - HF - H_2O (75°)

K_2CbF_7 - KF - HF - H_2O (25°)

The results are summarized in the attached 3 tables. On the basis of these results, the following procedure for the separation of columbium and tantalum seems to be advisable.

The mixture of oxides is dissolved in hydrofluoric acid. The solution is evaporated to a small volume in order to remove excessive HF and is diluted with water until a content of 3% K_2CbF_7 /sic! should be CbF_5, H_2CbF_3, or unless potassium had been added /a concentration corresponding to 3% K_2CbF_7 is reached in the solution. The concentration of HF at this point must not exceed 1-2%. Now enough KF (or a corresponding quantity of K_2CO_3 + HF) is added to supply a quantity required for the formation of potassium double fluorides of both metals and to leave over a 2% excess in solution. K_2TaF_7 which precipitates at this stage is filtered and washed with dilute HF. The filtrate is evaporated until crystallization of $K_2CbOF_5.H_2O$ begins and this crystallization is expedited by cooling. The crystals are filtered off. The crude crystals of both K_2TaF_7 and $K_2CbOF_5.H_2O$ are recrystallized from 1-2% HF. The first filtrate from $K_2CbOF_5.H_2O$ is added to a new portion of the initial mixture and the procedure described above is repeated.

Data on solubilities in HF at 75° are required in order to determine the optimum conditions for recrystallization.

Submitted May 27, 1946.

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2. Laubengayer and Felmer, J. Am. Chem. S, Vol. XIII, 3264, 1941.

3. Marignac, Ann. Chim. Phys., 8 (4), 9 (1966).

4. Ruff u. Schiller, Z. anorg. Ch., Vol. XIII, 329, 1911.

5. Zverev, and Meerson, Tsvetnye Metally (Non-Ferrous Metals), Vol. VIII, 97, 1939.

6. Babaeva and Klyachko-Gurvich, Zh. Obshchey Khimii, Vol. II, 220, 1924.

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Table 1. Solubility in the System K_2TaF_7 - HF - H_2O at 75°.

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No. of experiment.	Composition of saturated solutions in weight %			$\dfrac{\text{Mols HF}}{\text{Mols TaF}_5}$ in solution	Solid phase.
	HF	TaF_5	HF		
1.	2.70	3.20	1.52	2.25	
2	4.86	3.05	1.37	2.11	
3	7.12	3.25	-	-	
4	11.80	3.48	1.65	2.18	K_2TaF_7
5	21.52	5.15	-	-	
6	30.00	6.74	-	-	
7	35.50	10.87	4.69	2.08	

Table 2.   Solubility in the system $K_2Cr_2O_7$ - HF - H_2O at 25°.

No. of experiment.	Composition of saturated solutions in weight %				Solid phase
	HF	CrF_5	.F		
1	3.70	7.45	-	-	$K_2Cr_2O_7 \cdot H_2O$
2	5.00	..	..	...	$K_2Cr_2O_7 \cdot H_2O - K_2Cr_2O_7$
3	6..0	..	...	...	
4.	..0	1..0	-	-	
5	11.40	16.50	..	...	
6	15.60	....	-	-	CrF_5
7	20.20	11...	..	..	
8	20.70	11.05	...	...	
9	29.00	12.70	...	...	
10	32.10	1...4	...	..	
11	3..60	17...	-	-	

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